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12 a. DISTRIBUTION / AVAILABILITY STATEMENT

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12 b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Nanoscale Feature Development was the thrust of this program. Emphasis was on structures and mechanisms associated with material removal from semiconductor surfaces. The experiments were designed to examine the effects of point, line, and volume defects on material removal. To do this, native defects and those created by chemical and physical means were investigated, with emphasis on the modification of these defects by chemical and laser-assisted processes. The goal was to relate nanoscale defect development to atomic-level interactions. Scanning tunneling microscopy was used to achieve the spatial resolution needed.

The projects represented new opportunities and defined new challenges while capitalizing on prior ARO-sponsored research and laboratory development. The proposed experiments were unique in their emphasis on surface modification and the manipulation of nanoscale defect structures. They impact those who deal with material removal from surfaces, particularly from semiconductors. Several focused on fundamental mechanistic issues. While this program specifically discussed chemical etching by chlorine, the results are more general since similar effects would be expected under somewhat different processing conditions with bromine or iodine.

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List of manuscripts submitted or published:

1. J.H. Weaver and C.M. Aldao, "Spontaneous Halogen Etching of Si," in Morphological Organizations during Epitaxial Growth, edited by Z.Y. Zhang and M.G. Lagally (World Scientific Series on Directions of Condensed Matter Physics, 1999) pp. 453-484.

2. K. Nakayama, C.M. Aldao, and J.H. Weaver, "Vacancy-assisted Halogen Etching Si(100)-2x1," Phys. Rev. Lett. **82**, 568-571 (1999). See also Physical Review Focus, 21 January 1999 at <http://focus.aps.org/v3/st4.html>.

3. K. Nakayama and J.H. Weaver, "Electron-Stimulated Modification of Si Surfaces," Phys. Rev. Lett. **82**, 980-983 (1999). See also, Parity, 14, 44-46 (1999); Search & Discovery in Physics Today, 20 April 1999; and C&E News 77, 8-9 (January 25, 1999).

4. S. Jay Chey, L. Huang, and J.H. Weaver, "Interface Bonding and Manipulation of Ag and Cu Nanocrystals on Si(111)-(7x7)-based Surfaces" Phys. Rev. B **59**, 16033-16041 (1999).

5. K. Nakayama, C.M. Aldao, and J.H. Weaver, "Halogen Etching of Si(100)-2x1: Dependence on Surface Concentration and Vacancy Creation," Phys. Rev. B **59**, 15893-15901 (1999).

6. K.S. Nakayama and J.H. Weaver, "Si(100)-2x1 Etching with Fluorine: Planar Removal vs. Three Dimensional Pitting," Phys. Rev. Lett. **83**, 3210-3213 (1999).

7. B.Y. Han, K.S. Nakayama, and J.H. Weaver, "Electron and Photon-stimulated Modification of GaAs(110), Si(100), and Si(111)," Phys. Rev. B **60**, 13846-13853 (1999).

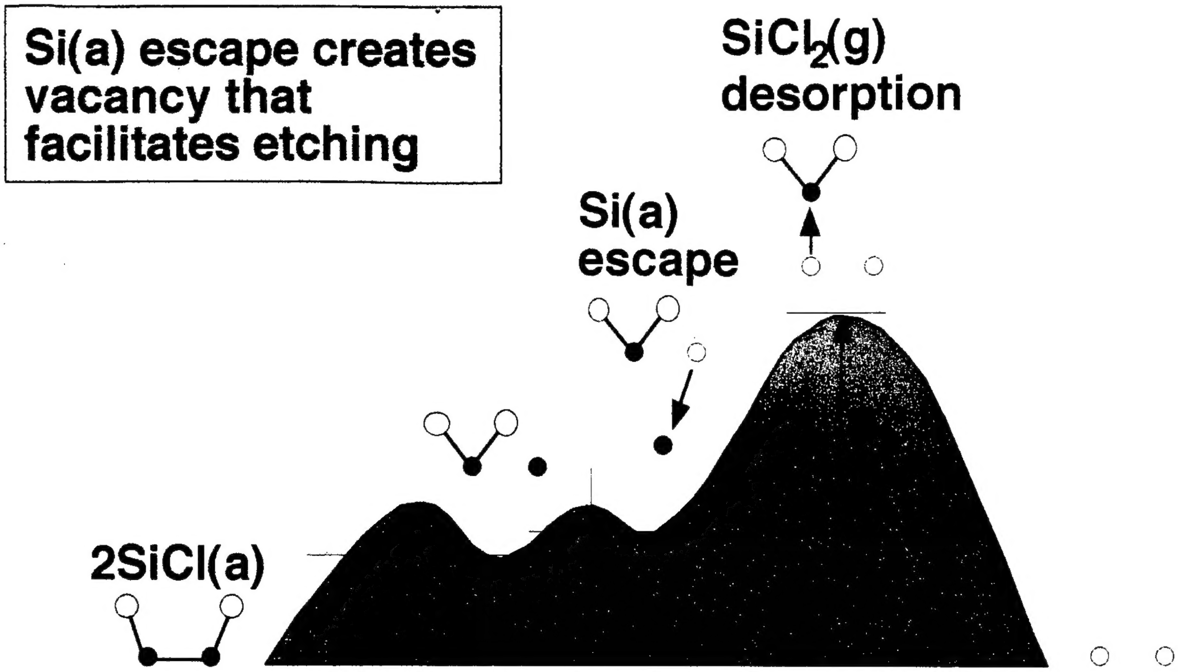
Scientific personnel supported by this project:

1. K. Nakayama, postdoc
2. B.Y. Han, postdoc

Scientific Progress and Accomplishments

Recent highlights have emphasized etching of Si(100) by Cl and Br and the modification of Si and GaAs surfaces by low energy electron beams. Both projects attracted attention in the popular scientific press.

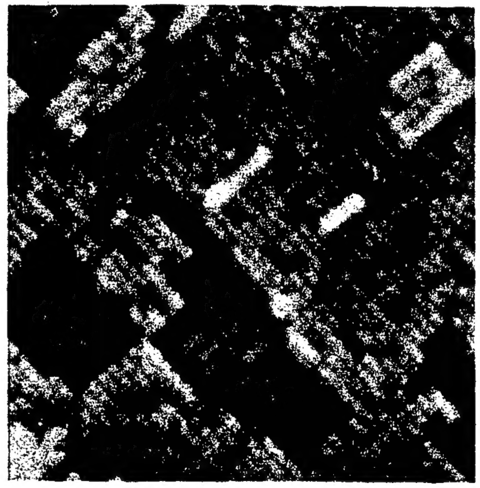
In the etching studies, we were able to determine the atomic step-by-step sequence of events that led to etching and nanoscale feature development. The results were featured in Physical Review Focus <http://publish.aps.org/FOCUS/v3/st4.html> under the title "New Theory of Etching." What was significant was that we showed that the sequence of events that controlled thermally-activated etching was different than generally believed.



The conventional description of etching involves the reaction 2SiCl → $SiCl_2$ + Si and then desorption of $SiCl_2$. In the potential energy surface above, this would imply direct desorption from the first well. However, the barrier for desorption is so large and the barrier against the reverse reaction is so small that there is very little chance for desorption.

Guided by calculations, however, we argued that the rate of desorption would be greatly enhanced if the reverse reaction problem were eliminated. This could be done by vacancy creation adjacent to the $SiCl_2$ species. This introduces a second well in the energy surface, as shown. Vacancy creation is depicted by "Si(a) escape" and it involves the transfer of the Si atom Si(a) onto the terrace. The lifetime of the $SiCl_2$ species is thereby increased since its decay pathway is eliminated.

To demonstrate that this new model was correct, we measured the etch rate as a function of surface coverage. This was important because the escape of the Si atom onto the terrace would be blocked as the surface becomes saturated by Cl. In this picture, the etch rate would reach a maximum at intermediate coverage and "more would not necessarily be better." This was just what we reported in Phys. Rev. Lett. **82**, 568 (1999). These results will significantly change the way the community views etching. Moreover, our results demonstrated that the surface is not a passive backdrop against which desorption occurs. Instead, it plays a pivotal role via defect creation and defect-assisted desorption.

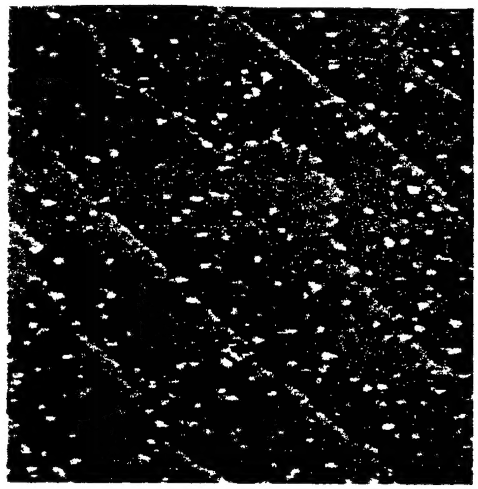


STM images like the above were used to demonstrate vacancy-assisted etching. They show patterning and nanoscale feature development, regrowth features on the main layer due to the Si atoms transferred there, and the bonding locations of residual Cl. Our etching work was further highlighted through a solicited feature article in Physics Today. The cover of the August issue was almost the following -- it lost in the final competition.

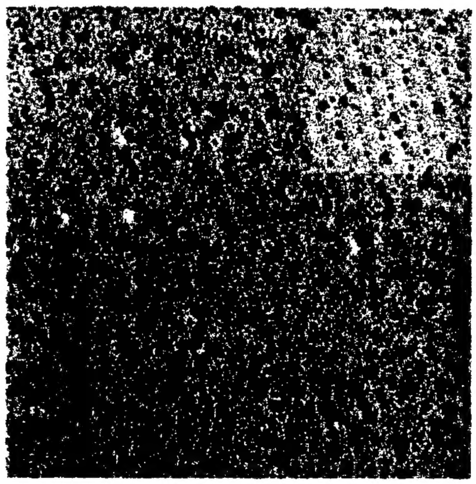
A second major advance during this reporting period dealt with electron-stimulated modification of surfaces. Whereas it is well known that electrons can induce desorption of chemisorbed atoms or molecules, can cause damage in ionic materials, and can be used to modify radiation-sensitive materials like polymers, it was accepted that low energy beams caused no damage to robust surfaces such as Si, GaAs, or other semiconductors. We used atomic resolution STM to test this accepted wisdom, and we demonstrated that it was wrong.

In a paper that recently [Phys. Rev. Lett. **82**, 980 (1999)], we showed the structural consequences of irradiation of Si(100) and Si(111) by 90-2000 eV electrons. We demonstrated vacancy creation associated with surface atom desorption and atom transfer onto the terrace. We also discussed the underlying physics behind surface modification. The two relevant processes involved resonant electron capture in an antibonding state or electron transfer from a bonding to an antibonding level of a surface atom. Both processes cause energy transfer from the electronic system to the nuclear system. This is needed if nuclear motion is to be accomplished.

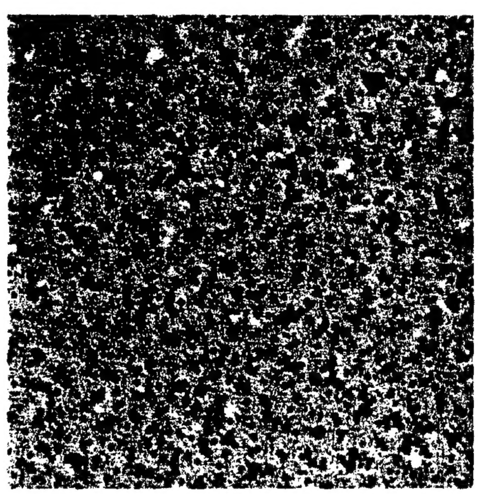
Surface modification by electrons was featured in Chemical & Engineering News (January 25, 1999, pp 8-9 and <http://pubs.acs.org/cgi-bin/bottomframe.cgi?7704notw3>). The following are images of the Si(100) and Si(111) surfaces before and after irradiation.



Si(100) after irradiation by 2000 eV electrons, showing defects and bright features that are due to Si atoms being transferred onto the terraces.



Si(111) before (inset) and after 90 eV electron irradiation. For this surface, vacancies are created by both desorption and transfer onto the terrace.



Si(111) after 2000 eV electron irradiation showing extensive surface modification. Such surfaces are substantially more reactive than the pristine surfaces.

In work that is ongoing, we are using low energy electrons to create point defects in the GaAs(110) surface and we are using photons from a 2.3 eV laser to expand those defects in the top layer. Our results show that layer-by-layer removal can be accomplished without using chemical etchants. In particular, damage from the electrons is limited to the top layer and desorption due to photon irradiation is limited to the perimeters of the pits, with no new pit formation. These results demonstrate new ways to accomplish nanoscale feature development.

Awards & Honors

- Medard W. Welch Award, American Vacuum Society
- Chief Judge, National Science Talent Search, Singapore
- R&D 100 Awards Judge
- National Research Council Advisory Board on Molecular Electronics
- Award Committee, International Union of Vacuum Science, Techniques, and Applications

Invited Talks

1. J.H. Weaver, "Nanostructures on Silicon: Synthesis, Integration, and Manipulation," 26th Conference on the Physics and Chemistry of Semiconductor Interfaces, La Jolla, January 1999. [Unable to attend.]

2. J.H. Weaver, "Challenges in Materials Science," National Science Talent Search Award Ceremony, Singapore, April 1999.

3. J.H. Weaver, "Atomic Processes at Surfaces: Visualization with Scanning Tunneling Microscopy," 12th Kongsberg Seminar, Kongsberg, Norway, May 1999.

4. J.H. Weaver, Plenary Lecture on the Uses of Photoemission, Workshop on Optical and Electron Spectroscopies, Mexico City, June 1999. [Unable to attend.]

5. J.H. Weaver, "Nanostructures and their Interactions," Fifth International Conference on Advanced Materials, International Union of Materials Research Societies, Beijing, June 1999. [Unable to attend.]

6. J.H. Weaver, "The Formation of Nanoclusters and their Interaction with Surfaces," Gordon Conference on Dynamics at Surfaces, Andover, New Hampshire, August 1999.

7. J.H. Weaver, "Semiconductor Surface Modification with Electrons and Photons, Viewed with Scanning Tunneling Microscopy," ECOSS-18, Vienna, Austria, September 1999.

8. J.H. Weaver, "Halogen Etching of Si with Emphasis on Atomic-Scale Processes," 46th International Symposium of the American Vacuum Society, Seattle, October 1999 [Medard W. Welch Award Presentation].